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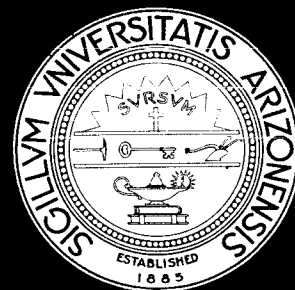
Stuart A. Hoenig
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FOURTH SIX-MONTH REPORT
January 1, 1965 - June 30, 1965

NsG-458

ENGINEERING RESEARCH LABORATORIES

COLLEGE OF ENGINEERING
UNIVERSITY OF ARIZONA
TUCSON, ARIZONA

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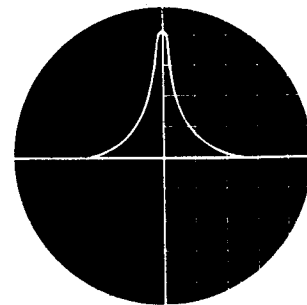

NsG-458

DETECTION TECHNIQUES FOR TENUOUS PLANETARY ATMOSPHERES

TO

Stuart A. Hoenig, Project Director
Melvin M. Eisenstadt, Graduate Associate
Charles W. Carlson, Graduate Assistant

Field Emission and Space Systems Laboratory
Department of Aerospace and Mechanical Engineering
The University of Arizona
Tucson, Arizona

ABSTRACT

A field ionization detector for water vapor (range $5 \cdot 10^{-6}$ - 10^{-3} torr) has been developed. Tests in (CO) and N_2 + H_2O mixtures indicate almost no sensitivity to (CO) and no sign of the formation of (NH_3) from (N_2) and (H_2O).

A chemisorption detector for water vapor has been developed, (range 10^{-8} - 10^{-4} torr). This detector is sensitive to (CO) and can be used as a detector for (CO) in vacuum systems. This system can operate in a hydrocarbon atmosphere.

A surface ionization detector for (H_2) in air has been developed, (range 0.5% to 4.5%). A similar detector for (CO) in air is under study.

Results on the chemisorption of (H) versus (H_2) on palladium are given. It is possible to separate the effects of (H) versus (H_2).

I. INTRODUCTION

This report will cover the work performed at The University of Arizona Field Emission and Space Systems Laboratory between January 1, 1965 and June 30, 1965 on Contract NsG-458. This contract was originally set up to cover the development of new types of instrumentation for lunar and planetary exploration. The work under way and project status to date will be reviewed in several separate sections below.

II. CHEMISORPTION DETECTOR FOR HYDROGEN

Completed in 1964 and published in The Review of Scientific Instruments for January 1965. Present range 10^{-5} to 10^{-8} torr; future plans call for an extension of range from 10^{-4} to 10^{-9} torr.

Our first attempts to extend the useful range of the detector by using a palladium-coated tungsten filament were unsuccessful. A thicker palladium coating is being applied to the filament and we hope this will solve the problem.

III. DETECTORS FOR WATER VAPOR

In our last report we discussed the detection of water vapor and the two possible approaches to this problem.

A. Field Ionization

The field ionization detector has been tested and we indicated in our last report that it operates over the range from $5 \cdot 10^{-6}$ to 10^{-3} torr of water vapor.

The detector has been tested in (CO) and no response was detected except at the very highest (CO) pressures (10^{-4} torr). This is somewhat surprising since (CO) has a dipole moment within a factor of 18 of water (CO = 0.1), H_2) = 1.85). Apparently the condensation effect[1,2] of water

is most important in the ionization phenomena.

The interaction between (N_2) and (H_2O) appears to be no problem over any reasonable range of (N_2, H_2O) pressures. Certain new pieces of apparatus will be needed for exploration of (N_2, H_2O) pressures above 10^{-3} torr. We hope to have this apparatus in operation in the fall of 1965.

We have had further correspondence with Dr. Beckey of the University of Bonn (Germany). He suggested that we use platinum rather than tungsten tips and a forty-tip platinum emitter has been designed and built.

Tests with this system have indicated that it operates properly but we must provide for careful control of the distance between the tips and the collecting screen. A new ionizer system will provide for micrometer control of the tip-to-screen distance. We hope to construct this apparatus during the summer of 1965 and test it in the fall of 1965. This will permit more accurate calibration of the detector as well as providing higher ion currents.

In our last report we indicated that the noise level in the field ionizer increased at low water vapor pressures ($< 10^{-5}$ torr). In his patent on the field ionization source (US-345407) Beckey discusses this and suggests methods for reducing this noise problem.

Our experiments with a pulse ionization system have not yet been successful but if necessary, the noise can be reduced by the electronic methods Beckey suggests.

B.   Thoriated Tungsten Filament Chemisorption Detector for Water Vapor

The results of this detector with water vapor were discussed in our last report. It was indicated that the detector operated from 10^{-4} to 10^{-8} torr of water vapor. Tests of this detector in (CO) indicate that there is some response to (CO). However, it is an increase rather than a

decrease in current as is the case for (H_2O).

The reaction of carbon monoxide on the thoriated tungsten filament is a complex one which depends upon filament temperature and previous exposure to water vapor. By operation at the proper temperature it is possible to separate the effects of (CO) from the effects of (H_2O). In Fig. 1 we show a calibration curve of the response of the detector to (CO). We do not plot a signal to noise ratio in this case since the base current is not a noise current but is dependent upon the temperature of the filament.

Since (CO) is a common residual gas in vacuum systems, a detector for (CO) may be useful in vacuum research. We hope to explore this in a future study.

The chemisorption detector for water vapor may have special utility for the detection of water vapor in the presence of hydrocarbon gases. A series of tests in methane have indicated that the detector is sensitive to as little as 10^{-7} torr of water vapor in the presence of 10^{-3} torr of methane.

Further work on this detector will be planned when the results of the Mars Mariner IV experiment are available.

IV. SURFACE IONIZATION DETECTOR FOR HYDROGEN

Since our last report this detector has been carefully calibrated over the range from 0.5 per cent $H_2/_{air}$ to 4.5 per cent $H_2/_{air}$ by volume. This response is quite linear and reproducible. The detector operates equally well in H_2/N_2 or $H_2/_{air}$ mixtures making it useful in situations where combustion-type detectors cannot operate.

The results of this work have been submitted to The Review of Scientific Instruments. A typical calibration curve is shown in Fig. 2.

Plans are under way to increase the sensitivity of this detector by enlarging the ionizing surface and it should be possible to operate at H_2/air ratios below 0.1 per cent quite easily.

At present, there is no good theoretical understanding of the surface ionization process. A careful search of the literature[3,4,5] reveals somewhat conflicting opinions and some authors[5] question that the effect even exists. In order to settle this debate we are building a small mass-spectrometer similar to that described in Ref. 6. This will permit analysis of the ions from the heated Pd surface.

V. CHEMISORPTION DETECTOR OF H VERSUS H_2

The differential chemisorption of (H) versus (H_2) has been measured on palladium and the results are shown in Fig. 3. It is somewhat surprising at first that (H) atoms are less active in chemisorption than (H_2) molecules. However, this can be understood if we consider the processes involved in the experiment.

The hydrogen beam impinged upon a hot ($1000^{\circ}C$) palladium filament, and a fraction of the beam was chemisorbed. This chemisorption resulted in a lowering of the palladium work function[7]. Therefore, the thermionic emission current from the filament increased as the hydrogen coverage increased.

The thermionic emission current was measured by collecting the electrons released from the filament on a positively biased grid. Raw data was taken in the form of beam source pressure vs. thermionic emission current (I). The thermionic emission current was then normalized by dividing it by (Io), where (Io) was the thermionic emission current with the beam not operating. Thus, (Io) represents the emission current from the filament

when the filament was in a vacuum environment (about 10^{-9} torr). The beam source pressure was converted to a quantity called "equivalent hydrogen pressure" (Pe). By "equivalent hydrogen pressure" it is meant that the number of gas particles impinging on the filament per cm^2 per second from the beam is the same as the impingement rate per cm^2 when the filament is enveloped in a gaseous environment at a pressure (Pe). The results (I/I_o) vs (Pe) are shown in Fig. 3 for both atomic and molecular beam operation.

The molecular beam data agrees well with the results of Ref. 7, which it should. The most significant piece of information in the figure is the fact that more hydrogen is chemisorbed from the molecular beam than from the atomic beam. The limits of free molecular flow are shown in Fig. 3. These limits represent the points at which the mean free path of the hydrogen in the beam source was ten times the diameter of the beam orifice. Curve 1 is plotted somewhat beyond this point.

If one considers a hydrogen molecule striking the surface, the following mechanisms will probably occur:

1. The molecule is physically adsorbed on the surface with a small heat of adsorption (~ 0.2 k cal/mole).

2. The surface imparts enough energy to the molecule to dissociate it (103 k cal/mole).

3. The two dissociated hydrogen atoms are then chemisorbed, with a heat of adsorption of about 65 k cal/mole[8].

For the atomic beam case, only Step 3 is necessary. Thus, it might appear that more hydrogen should be adsorbed from the atomic beam.

However, one more effect must be considered. In order for an atom to be chemisorbed, the kinetic energy which the atom possesses when

it strikes the filament must be transferred to the filament in a short time, otherwise the atom will leave the surface. This problem has been considered by Zwanzig[9] and also by McCarroll and Ehrlich[10]. They conclude that there is a maximum kinetic energy which an impinging particle may have if it is to be adsorbed. If it possesses more kinetic energy than this critical amount, it will not be adsorbed. The data in Fig. 3 can be explained in terms of this collision-energy picture. A more detailed discussion will be given in our next report.

VI. FIELD-IONIZATION MASS SPECTROMETER SOURCE

In our last report we mentioned the prospect of a field ionization source of a mass-spectrometer. This would be a natural outgrowth of the work done on a field ionization detector for water vapor (Section III).

We have had some extensive correspondence with Dr. Beckey on this point and it is clear that he has already carried the technique to the development of a commercial instrument. It is our feeling that this type of ion source will be of great importance in the future and will eventually replace electron ionization entirely.

In order to gain some competance in this field we have begun the design and construction of a small mass-spectrometer similar to the design reported in Ref. 6. This instrument will have permanent magnets and will be swept in $(\frac{e}{m})$ ratio by varying the applied electric field. This instrument will also be used for studies of positive ion emission from metal surfaces, Sections IV and VII.

VII. SURFACE IONIZATION DETECTOR FOR CARBON MONOXIDE

During the calibration of the surface ionization detector for hydrogen we checked the response of the instrument to a series of other

gases, i.e., (O_2), (N_2), methane, (CO_2), and (CO). There was no significant response to any of these gases, except (CO).

(CO) behaves chemically like hydrogen so the response was not too surprising. Since (CO) is a difficult gas to detect by existing techniques, a program to develop a surface ionization detector for CO was initiated. The results to date are shown in Fig. 4. Detection for (CO) is possible over a range from about 0.8 per cent CO/air to 4 per cent CO/air. This partially covers the range where (CO) becomes dangerous to human life. Calibration at higher CO/air ratios is possible but the explosive limit is 12 per cent and we dare not approach that with present equipment.

Our future plans call for improvement of this detector by development of a better ionization source to improve signal to noise ratio.

A (CO) detector might have a place in the Space Program for monitoring of vehicle environments. There may also be an interest in a device of this type for analysis of exhaust from automobiles. These applications will be explored under a separate program to be proposed to NASA. This program is expected to run concurrently with the present investigation. Both investigations will use similar apparatus and techniques so the joint program is a logical one.

VIII. LARGE U-H-V SYSTEM

In our last report we indicated that the 18 x 22 inch vacuum system had been installed and leak tested. This system is now ready-to-go and the first experiment will probably be an investigation of the variation of sticking coefficient with molecular velocity. We hope to use hydrogen atoms and molecules in this investigation to compare our results with those discussed in Section IV.

IX. CONCLUSIONS AND FUTURE PLANS

The development of new detectors seems to have made progress during this period. Two new detection devices were developed and submitted for publication. Other devices are in various stages of completion or development. A number of new directions for research have been indicated and it will be necessary to choose the most fruitful areas for our future efforts.

The program is now entering a new phase of activity in the sense that the growth period, of seeking new areas for research and developing techniques, is at an end. What must be done now is the hard choice of what research is most likely to yield useful results. For example, the hot filament detectors are most useful in certain areas but they are necessarily fragile, subject to burnout and generally poisoned by oxygen. The surface ionization systems seem to overcome some of these problems and for this reason we have begun to investigate this area more closely.
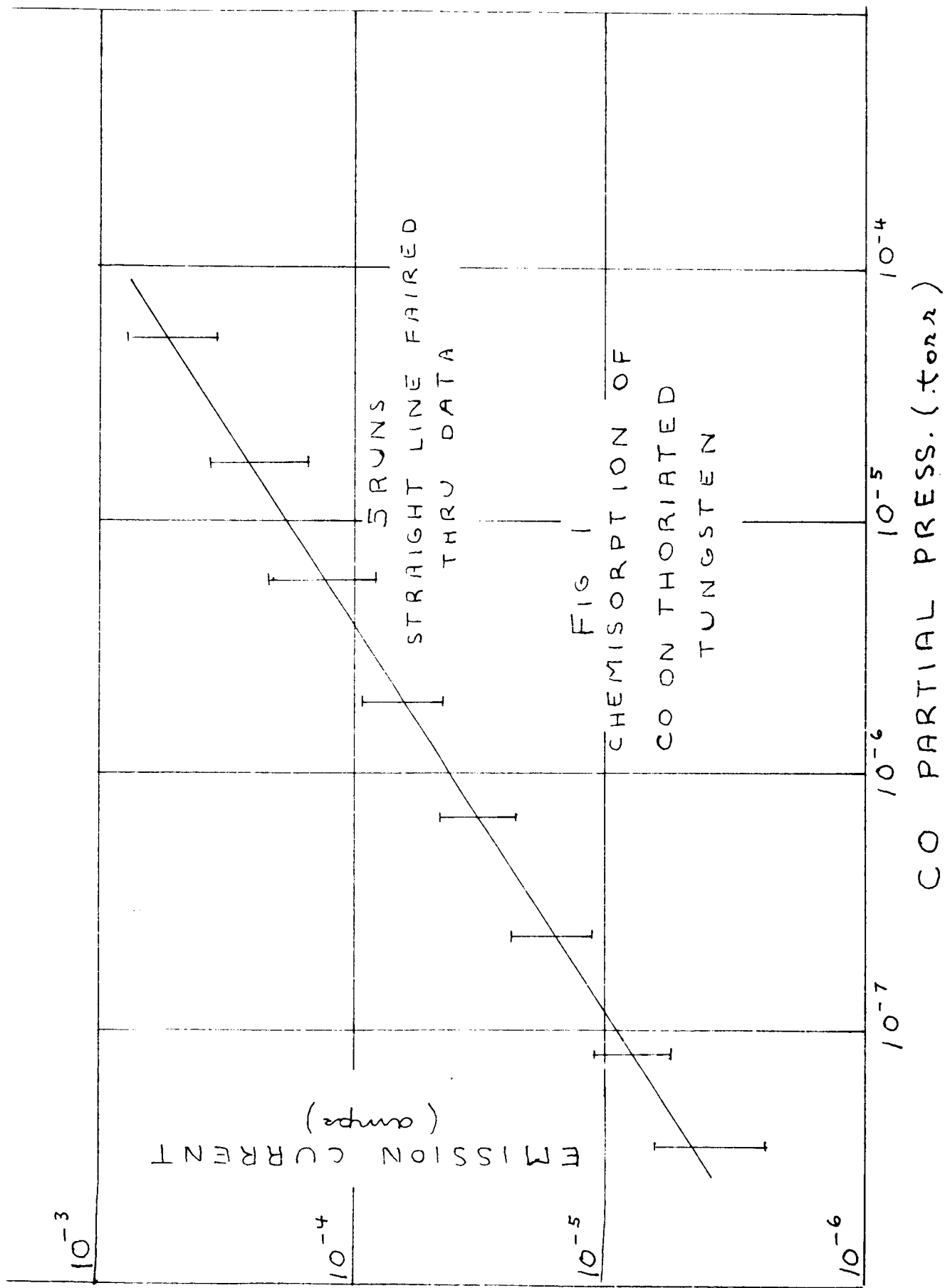
The area of mass-spectrometry is one which fits rather closely with the experience of our group and we hope to enter this area also.
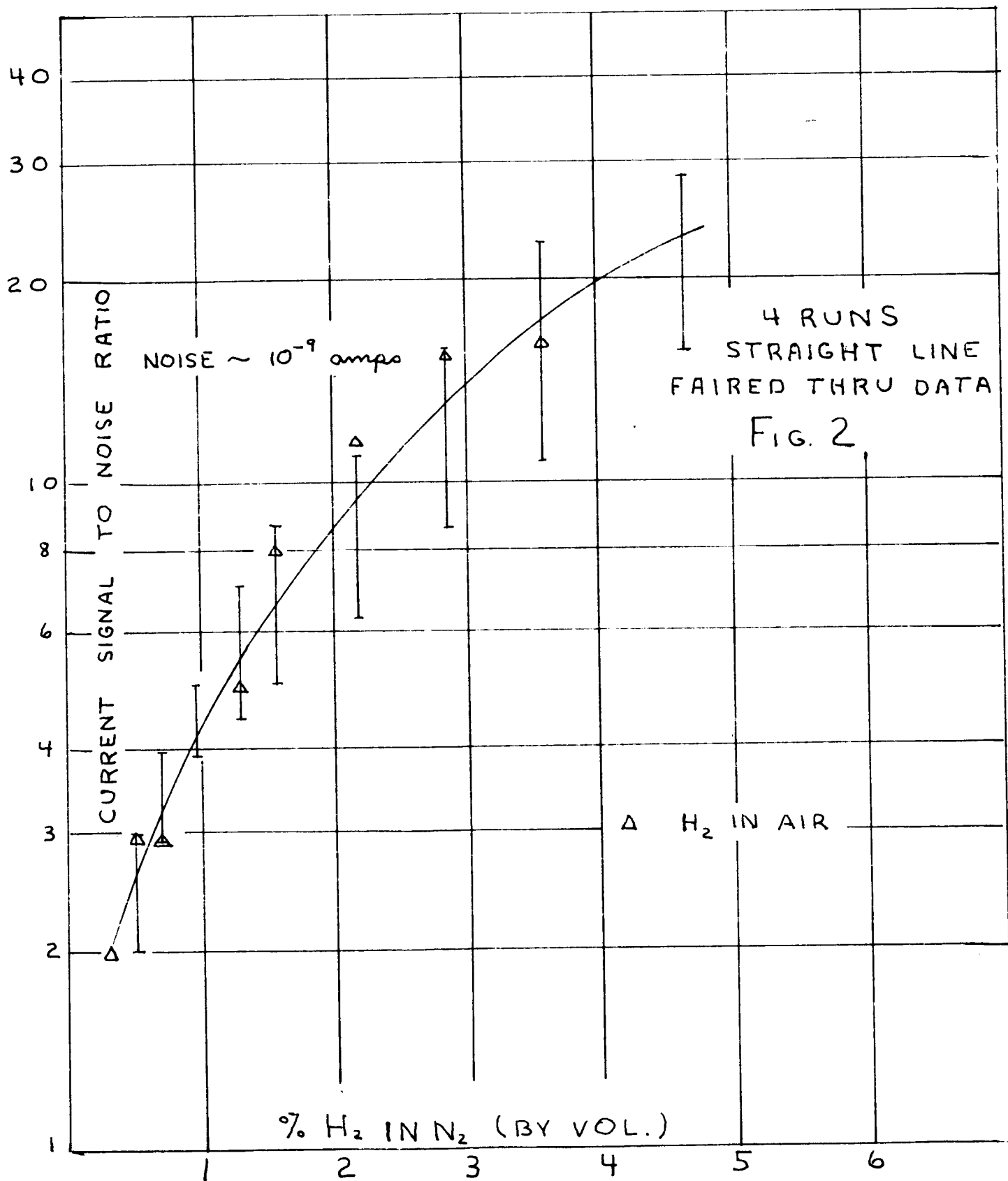
The chemisorption detector for water vapor is interesting and sensitive but unless a need arises for a detector that can operate in a hydrocarbon atmosphere we probably will not investigate it further.

It would be most useful to have some feedback from NASA on what detectors are needed. This would aid in planning future programs and areas of research.

REFERENCES

1. Beckey, H.,
   Field Ionization Mass Spectroscopy
   Advances in Mass Spectroscopy
   ed. Elliot, R., Pergammon Press, N. Y. p. 1, 1964.

2. Schmidt, Von W.
   Masspectrometric Investigations of the Field-Ionization of Water
   Vapor on Tips of Tungsten, Platinum and Iridium. (In German)
   Zeit. Für. Nature.,
   Band 19, Heft 3, pp. 318 (1964).

3. O. Richardson
   The Emission of Electricity from Hot Bodies
   Longmans Green and Company, New York, 2 ed. 1921, Chap. VI, VII.

4. C. Bachman, P. Silverberg
   Thermionic Ions from Hydrogen-Palladium
   J. Appl. Phys.
   29, No. 8, 1266-1267 (1958)

5. Yu. I. Belyakov, N. I. Ionov
   Pulsed Mass-Spectrograph Investigation of Desorption of Hydrogen
   and Deuterium from Palladium
   Zh. Tekh. Fiz. (In Russian)
   30, No. 2, 216-222 (1960).

6. J. Carette, L. Kerwin
   Small Fringe-Field-Free Mass Spectrometer
   Rev. Sci. Instr.
   36, No. 4, 537-539 (1965)

7. Eisenstadt, M., Hoenig, S.
   Chemisorption Detector for Hydrogen
   Rev. Sci. Instr.
   36, 66, (1965)

8. Ehrlich, G.
   Molecular Dissociation and Reconstitution on Solids
   J. Chem. Phys.
   31, 1111 (1959)

9. Zwanzig, R.
   Collision of a Gas Atom with a Cold Surface
   J. Chem. Phys.
   32, 1173 (1960)

10. McCarroll, B., Ehrlich, G.
    Trapping and Energy Transfer in Atomic Collisions with a Crystal Surface
    J. Chem. Phys.
    38, 523 (1963)

FIG. 1
CHEMISORPTION OF
CO ON THORIATED
TUNGSTEN

STRAIGHT LINE FAIRED
THRU DATA

5 RUNS

EMISSION CURRENT
(amps)

CO PARTIAL PRESS. (torr)

10^{-3} 10^{-4} 10^{-5} 10^{-6}

10^{-7} 10^{-6} 10^{-5} 10^{-4}

Fig. 2 — Current signal to noise ratio vs. % H₂ in N₂ (by vol.). NOISE ~ 10^{-9} amps. 4 RUNS STRAIGHT LINE FAIRED THRU DATA. △ H₂ IN AIR.

FIG. 3

EQUIVALENT HYDROGEN PRESSURE (P, ~ torr)

$I/I_o = SIGNAL/NOISE$

curve 1, 2 runs, filament at 1000°C, oven at 300°K, Io = 1.4 x 10⁻¹¹ amps

curve 2, 2 runs, filament at 1000°C, oven at 2400°K, Io = 1.7 x 10⁻¹¹ amps

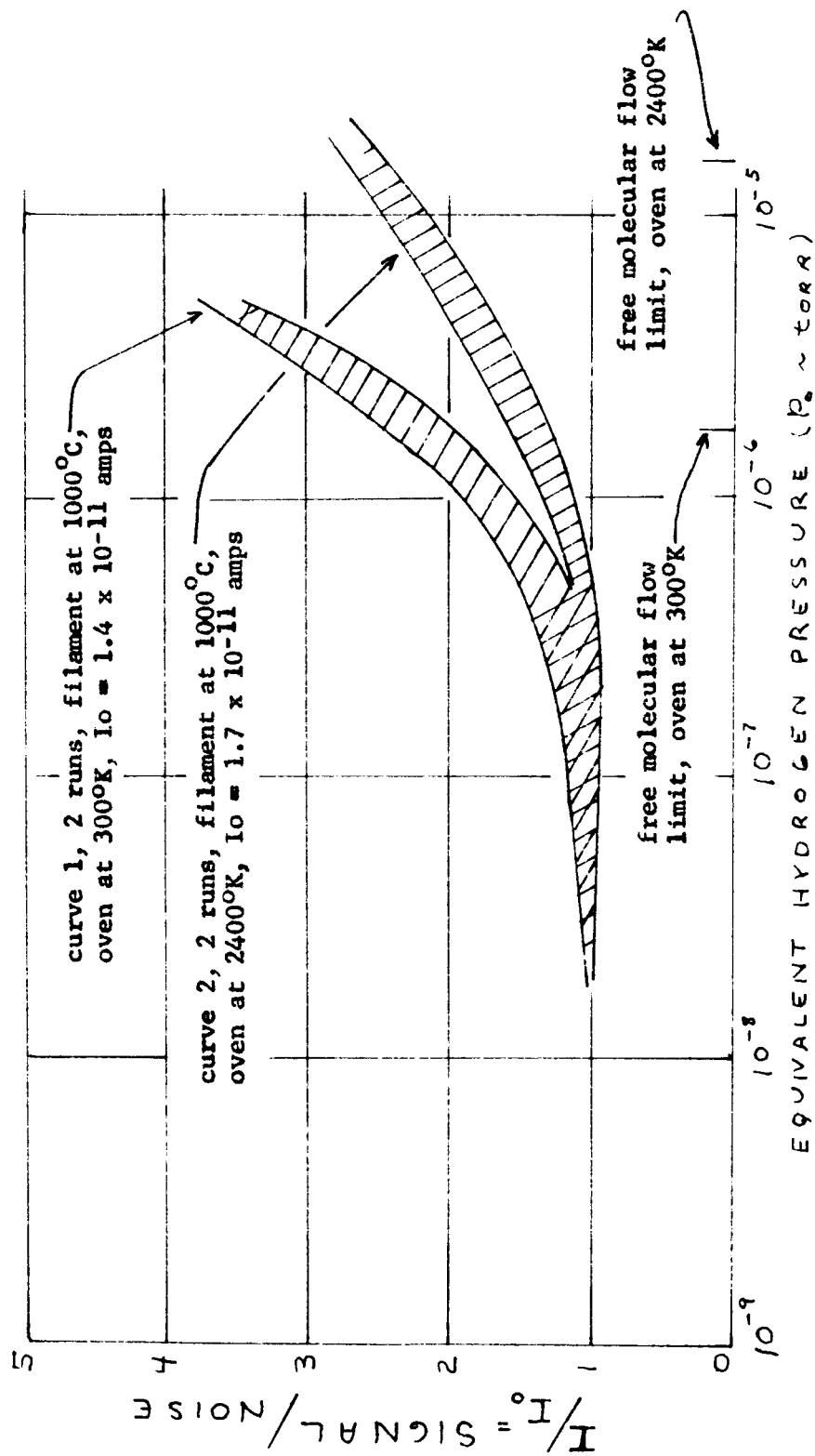free molecular flow limit, oven at 2400°K

free molecular flow limit, oven at 300°K

Normalized emission current vs equivalent hydrogen pressure at a filament temperature of 1000°C and oven temperatures of 300°K and 2400°K. Data from filament No. 2.

NOISE ~ 10^{-9} amps = I_o

4 RUNS
STRAIGHT LINE
FAIRED THRU
DATA

FIG 4

CO SURFACE IONIZATION
DETECTOR

% CO IN AIR BY VOL.

I/I_o SIGNAL/NOISE